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Photophysical and photochemical properties of a family of isoelectronic tris chelated ruthenium(II) aza-/azo-aromatic complexes

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We have investigated the electrochemical, spectroscopic and electroluminescent properties of a family of aza-aromatic complexes of ruthenium of type $[\text{Ru}^{\text{II}}(\text{bpy}/\text{phen})_2(\text{L})]^{2+}$ ($4d^6$) with three isomeric L ligands, where, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline and the L ligands are 3-(2-pyridyl)[1,2,4]triazolo[1,5-a]pyridine (L^1), 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine (L^2) and 2-(2-pyridyl)[1,2,4]triazolo[1,5-a]pyridine (L^3). The complexes display two bands in the visible region near 410–420 and 440–450 nm. The complexes are diamagnetic and show well defined ^1H NMR lines. They are electroactive in acetonitrile solution and exhibit a well defined $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple near 1.20 to 1.30 V and -1.40 to -1.50 V due to ligand reduction *versus* Saturated Calomel Electrode (SCE). The solutions are also luminescent, with peaks are near 600 nm. All the complexes are electroluminescent in nature with peaks lying near 580 nm. L^1 and L^3 ligated complexes with two bpy co-ligands show weak photoluminescence (PL) but stronger electroluminescence (EL) compared to corresponding L^2 ligated analogues.

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Introduction

The past few years have seen a rapid development in the chemistry, biochemistry and photophysics of aza-aromatic complexes of ruthenium. Aza-aromatic complexes of ruthenium are extensively used as photosensitizers, for production of H_2 and O_2 from H_2O ,^{1–5} and for biological sensing.^{6,7} Cyclic aza-aromatic complexes of ruthenium are used as sensitizers in dye-sensitized solar cells.^{8–14} Aza-aromatic ruthenium(II) complexes are also promising candidates for incorporating into low voltage, single-layer, solid-state electroluminescent devices, such as light emitting diodes (LEDs), as they have high photo-redox efficiencies.^{15–33}

Electroluminescent devices using transition metal dyes typically use unsubstituted and peripheral hydrogen substituted polypyridyl complexes of ruthenium and other transition metal complexes.³⁴ However, nitrogen rich heterocyclic ligands, complexing with platinum, iridium and other transition metals, have been extensively used to synthesize light-emitting self-assembled materials.^{35,36} In order to explore the activity of nitrogen rich heterocyclic ligands in electroluminescent devices, we developed three isomeric triazolopyridine ligands (L^1 – L^3) and their ionic ruthenium dye

complexes with bipyridine or *o*-phenanthroline co-ligands. The complexes display two $\pi(\text{Ru})$ – $\pi^*(\text{L})$ metal to ligand charge transfer (MLCT) excitation bands of moderate intensity in the visible region, near 410–420 and 440–450 nm, in addition to the standard heterocyclic UV region band in acetonitrile. The solutions are also luminescent, with absorbance peaks near 600 nm. Excitation spectral studies have demonstrated that the luminescence is associated with the above noted MLCT bands. The redox behavior in acetonitrile are characterized through a one-electron oxidation of the ruthenium center at 1.20–1.30 V and a one electron reduction of the ligand at -1.40 – -1.50 V *versus* saturated calomel electrode (SCE).

Experimental section

Materials

$[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Ru}(\text{phen})_2\text{Cl}_2]$ were prepared as reported earlier.³⁷ For electrochemical work HPLC grade acetonitrile was used. All other chemicals and solvents were of reagent grade and were used as received.

Physical measurements

^1H and ^{13}C NMR spectra were recorded with a Bruker FT 300 MHz spectrometer. Spin-spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet. Electrochemical measurements were performed under nitrogen atmosphere using a CH 620A electrochemical analyzer, with platinum

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working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the potentials were referenced to the saturated calomel electrode (SCE) without junction correction. Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 series II analyzer. Mass spectra were measured with Q-TOF mass spectrometer (MeCN). UV-vis absorption spectra and fluorescence spectra of the ruthenium complexes in acetonitrile solution were recorded with a UV-1601 PC spectrophotometer and Perkin-Elmer model LS 55 luminescence spectrometer respectively. The solutions used for emission and life time measurements were de-aerated by bubbling nitrogen gas for 30 min. Fluorescence life times were determined from time-resolved intensity decay by the method of time-correlated single-photon counting using a picoseconds diode laser (IBH, UK, nanoled-07) as the light source. The decays were analyzed using IBH DAS-6 decay analysis software.

Determination of quantum yield (Φ)

Quantum yields were determined by comparing with a $[\text{Ru}(\text{bpy})_3]^{2+}$ standard ($\Phi_s = 0.042$) measured in aqueous solution.³⁸ The relevant formula is given in the following equation:

$$\Phi_x = [\Phi_s(A_s \times I_x)/(A_x \times I_s)](\eta_x/\eta_s)^2 \quad (1)$$

here x and s subscripts refer to the experimental sample and standard respectively. A is the absorbance (set near 0.1 in a 1 cm cell) at the peak (436 nm in the case of the standard), I is the area under the emission spectrum and η is the refractive index of the solvent used.

Electroluminescence study

Light emitting devices were fabricated on indium tin oxide (ITO) coated glass substrates, which were cleaned and processed following standard protocol. Ruthenium complexes were first dissolved in acetonitrile (2 mg ml⁻¹) and were spin coated on the ITO-coated glass substrate at 2000 rpm for 60 s. The films were dried for 12 h at 110 °C under vacuum oven (10⁻³ Torr). The thicknesses of the films were around 75 nm (as measured by a Planar Products Limited SF101 surfometer). Aluminium (Al) was vacuum-evaporated on top of the annealed films from a tungsten filament basket at a pressure below 10⁻⁵ Torr. Active area of each of the devices was 6 mm². The electrical characteristics of the devices were measured in a shielded vacuum chamber with a Yokogawa 7651 dc source and a Keithley 486 picoammeter. The radiance of the devices were measured with a Keithley 617 electrometer, and a Si photodiode (Centronics Co. OSD100-5T). ITO was used as the anode for all electrical measurements. The electroluminescence spectra were measured with a Horiba Jobin Yvon (Fluoromax-3) luminescence spectrometer. The instruments were controlled with a personal computer *via* a general-purpose interface bus (GPIB).

Synthesis of ligands

L¹ and L² ligands were prepared by literature methods while ligand L³ was prepared slightly modifying the literature method.^{38–41}

Synthesis of ligand (L³)

2-Cyanopyridine (500.00 mg, 4.76 mmol) was condensed with 2-aminopyridine (452.00 mg, 4.76 mmol) to form *N*-(2-pyridyl)-2-pyridinecarboamide and then the product was added to a mixture of acetic acid and acetic anhydride (1 : 1) at 0 °C. The solution was then brought to room temperature and stirred for 2 h. The solution was then refluxed for 2 h. The resulting compound was then treated with dil. HCl with aq. NaOCl. Yield: 518.00 mg (55%). ¹H NMR (CDCl₃), δ 8.65 (triazolofused-py-H6, 1H, d, J = 4.68 Hz), 8.43 (triazolofused-py-H3, 1H, d, J = 8.37 Hz), 7.91 (triazolofused-py-H4, 1H, t, J = 9.01 Hz), 7.77 (triazolofused-py-H5, ¹H, t, J = 8.75 Hz), py-protons: 8.37 (py-H6', 1H, d, J = 6.57 Hz), 8.29 (py-H3', 1H, d, J = 7.56 Hz), 7.50 (py-H4', 1H, t, J = 9.91 Hz), 7.08 (H5', 1H, t, J = 9.95 Hz).

Synthesis of complexes

Five complexes were synthesized by the same general procedures and the details are described for one complex.

$[\text{Ru}(\text{bpy})_2(\text{L}^2)](\text{PF}_6)_2$, II: L² (40.58 mg, 0.207 mmol) was added to a hot solution of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (100 mg, 0.207 mmol) in ethanol. On subsequent heating under reflux for 1 h, the solution color changed from reddish brown to orange. The volume of the solvent was reduced under reduced pressure, and ammonium hexafluorophosphate (NH₄PF₆) was added to solution. The orange microcrystalline product was collected by filtration. The solid mass thus obtained was repeatedly washed with ethanol and ether. The solid was dissolved in minimum volume of acetonitrile and subjected to chromatography on a silica gel column (10 × 1 cm, 60–120 mesh) prepared in toluene. The complex was eluted with acetonitrile–toluene mixture (1 : 1). Yield = 134.07 mg (72%). ¹H NMR (CD₃CN) δ 8.66 (triazolofused-py-H6, 1H, d, J = 7.07 Hz), 8.48 (triazolofused-py-H3, 1H, d, J = 8.70 Hz), 8.42 (triazolofused-py-H4, 1H, t, J = 7.92 Hz), 8.31 (triazolofused-py-H5, ¹H, t, J = 7.54 Hz), py-protons: 8.44–7.31, ¹³C NMR (CD₃CN) δ 157.56, 157.51, 157.31, 152.56, 152.46, 152.24, 152.22, 138.45, 138.29, 138.28, 138.16, 138.15, 138.08, 130.95, 129.90, 128.02, 127.96, 127.94, 127.88, 127.24, 127.02, 125.41, 124.69, 124.56, 124.23, 123.93, 122.30, 122.12, 118.46, 117.75, 117.18. MS (m/z , ESI), 755.08 (:M – PF₆ + H⁺), 304.91 (:M – 2PF₆). Elemental analysis calculated for C₃₁H₂₄N₈RuP₂F₁₂: C, 41.39, H, 2.69, N, 12.46 found: C, 41.13, H, 2.57, N, 12.28.

$[\text{Ru}(\text{bpy})_2(\text{L}^1)](\text{PF}_6)_2$, I: L¹ (40.58 mg, 0.207 mmol) and 100 mg (0.207 mmol) $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ were employed. Yield = 147.10 mg (79%). ¹H NMR (CD₃CN) δ 8.86 (triazolofused-py-H6, 1H, d, J = 7.03 Hz), 8.47 (triazolofused-py-H3, 1H, d, J = 8.07 Hz), 8.44 (triazolofused-py-H4, 1H, t, J = 7.97 Hz), 8.41 (triazolofused-py-H5, 1H, t, J = 7.77 Hz), py-protons: 8.39–7.29, ¹³C NMR (CD₃CN) δ 153.32, 152.83, 152.79, 152.30, 152.21, 138.38, 138.26, 138.11, 138.05, 137.89, 131.10, 127.93, 127.86, 127.83, 127.22, 126.82,

124.92, 124.67, 124.51, 124.04, 123.92, 122.77, 122.51, 122.35, 122.11, 122.01, 121.67, 118.28, 117.70, 117.33, 116.54. MS (m/z , ESI), 755.08 ($:\text{M} - \text{PF}_6 + \text{H}^+$), 305.05 ($:\text{M} - 2\text{PF}_6$). Elemental analysis calculated for $\text{C}_{31}\text{H}_{24}\text{N}_8\text{RuP}_2\text{F}_{12}$: C, 41.39, H, 2.69, N, 12.46 found: C, 41.10, H, 2.47, N, 12.33.

$[\text{Ru}(\text{bpy})_2(\text{L}^3)](\text{PF}_6)_2$, III: L^3 (40.58 mg, 0.207 mmol) and 100 mg (0.207 mmol) $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ were employed. Yield = 139.65 mg (75%). ^1H NMR (CD_3CN) δ 8.83 (triazolofused-py-H6, 1H, d, J = 7.00 Hz), 8.44 (triazolofused-py-H3, 1H, d, J = 8.13 Hz), 8.42 (triazolofused-py-H4, 1H, t, J = 7.92 Hz), 8.40 (triazolofused-py-H5, ^1H , t, J = 7.65 Hz), py-protons: 8.40–7.28, ^{13}C NMR (CD_3CN) δ 154.33, 153.14, 152.57, 152.31, 152.12, 138.31, 138.26, 138.01, 138.00, 137.83, 131.00, 127.64, 127.57, 127.33, 127.02, 126.21, 125.92, 124.45, 124.33, 124.09, 123.81, 122.77, 122.49, 122.41, 122.09, 122.02, 121.63, 119.01, 117.90, 117.76, 116.92. MS (m/z , ESI), 755.07 ($:\text{M} - \text{PF}_6 + \text{H}^+$), 305.06 ($:\text{M} - 2\text{PF}_6$). Elemental analysis calculated for $\text{C}_{31}\text{H}_{24}\text{N}_8\text{RuP}_2\text{F}_{12}$: C, 41.39, H, 2.69, N, 12.46 found: C, 41.11, H, 2.43, N, 12.23.

$[\text{Ru}(\text{phen})_2(\text{L}^1)](\text{PF}_6)_2$, IV: L^1 (36.85 mg, 0.188 mmol) and 100 mg (0.188 mmol) $[\text{Ru}(\text{phen})_2\text{Cl}_2]$ were employed. Yield = 121.14 mg (68%). ^1H NMR (CD_3CN) δ 8.86 (triazolofused-py-H6, 1H, d, J = 7.01 Hz), 8.52 (triazolofused-py-H3, 1H, d, J = 9.21 Hz), 8.47 (triazolofused-py-H4, 1H, t, J = 8.55 Hz), 8.43 (triazolofused-py-H5, ^1H , t, J = 7.00 Hz), py-protons and CH protons of phen: 8.42–7.10, ^{13}C NMR (CD_3CN) δ 157.55, 157.47, 157.31, 157.09, 153.33, 152.85, 152.80, 152.59, 152.31, 152.21, 147.7, 139.00, 138.39, 138.26, 138.11, 138.05, 131.11, 129.33, 128.22, 127.94, 127.88, 127.85, 127.23, 126.84, 124.94, 124.69, 124.52, 124.04, 123.92, 122.80, 118.74, 118.34, 117.74, 117.33, 116.13, 115.64. (m/z , ESI), 803.28 ($:\text{M} - \text{PF}_6 + \text{H}^+$), 329.14 ($:\text{M} - 2\text{PF}_6$). Elemental analysis calculated for $\text{C}_{35}\text{H}_{24}\text{N}_8\text{RuP}_2\text{F}_{12}$: C, 44.36, H, 2.55, N, 11.82 found: C, 44.13, H, 2.69, N, 11.71.

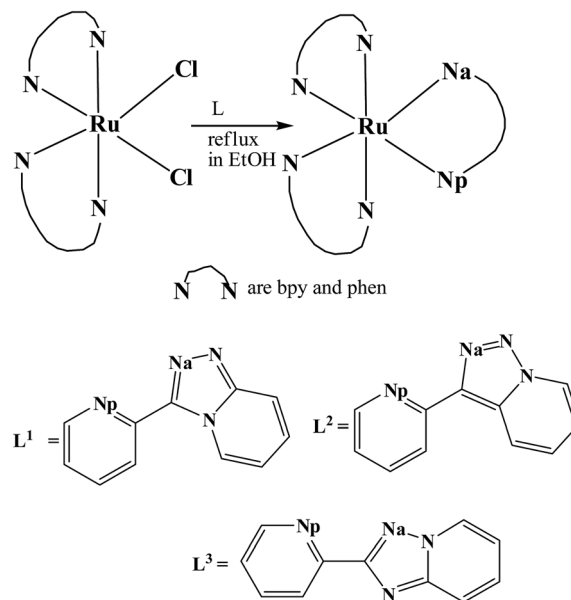
$[\text{Ru}(\text{phen})_2(\text{L}^2)](\text{PF}_6)_2$, V: L^2 (36.85 mg, 0.188 mmol) and 100 mg (0.188 mmol) $[\text{Ru}(\text{phen})_2\text{Cl}_2]$ were employed. Yield = 121.14 mg (68%). ^1H NMR (CD_3CN) δ 8.78 (triazolofused-py-H6, 1H, d, J = 7.13 Hz), 8.52 (triazolofused-py-H3, 1H, d, J = 8.00 Hz), 8.38 (triazolofused-py-H4, 1H, t, J = 7.55 Hz), 8.32 (triazolofused-py-H5, ^1H , t, J = 7.57 Hz), py-protons and CH protons of phen: 8.55–7.10, ^{13}C NMR (CD_3CN) δ 154.47, 153.99, 153.64, 153.49, 153.37, 153.32, 153.28, 152.76, 152.22, 139.03, 138.41, 138.22, 137.80, 137.26, 137.20, 137.01, 130.87, 129.42, 129.33, 128.65, 128.60, 128.54, 128.44, 128.32, 128.22, 126.91, 126.45, 126.39, 126.32, 125.70, 125.21, 122.23, 118.37, 117.74, 117.15. (m/z , ESI), 802.25 ($:\text{M} - \text{PF}_6$), 328.76 ($:\text{M} - 2\text{PF}_6$). Elemental analysis calculated for $\text{C}_{35}\text{H}_{24}\text{N}_8\text{RuP}_2\text{F}_{12}$: C, 44.36, H, 2.55, N, 11.82 found: C, 44.10, H, 2.67, N, 11.66.

Results and discussions

Synthesis

Three isomeric ligands (L^1 – L^3) were synthesized, which, in addition to bpy and phen co-ligands, vary in position of nitrogen and fused pyridine ring. The heteroleptic $\text{Ru}(\text{II})$ ($4d^6$) complexes I–V were synthesized by refluxing $[\text{Ru}(\text{bpy}/\text{phen})_2\text{Cl}_2]$ with L in boiling ethanol for an hour. The orange colored $[\text{Ru}(\text{bpy}/\text{phen})_2\text{L}]^{2+}$ were precipitated with an excess of NH_4PF_6

and purified by column chromatography on silica gel, using a mixture of acetonitrile and toluene.



Spectra and electrochemistry

In addition to standard aza-aromatic signatures in the UV region, the complexes (in acetonitrile) display bands of moderate intensity in the visible region near 410–420 and 440–450 nm (Table 1), similar to standard $\text{Ru}(\text{bpy})_3$ complexes.²⁸ The spectra of the complexes are displayed in Fig. 1. These bands have been assigned to $d(\text{Ru})-\pi^*(\text{L})$ MLCT transitions. The complexes display well-resolved ^1H and ^{13}C NMR in CD_3CN solution. The ^1H NMR and ^{13}C NMR spectra of the complexes have peaks corresponding to the six-membered and five-membered azo-aromatic protons and carbons, at 8.90 to 7.10 ppm and at 160 to 115 ppm respectively, as has been observed in literature.^{38,39,42–44} The NMR data are given in the experimental section.

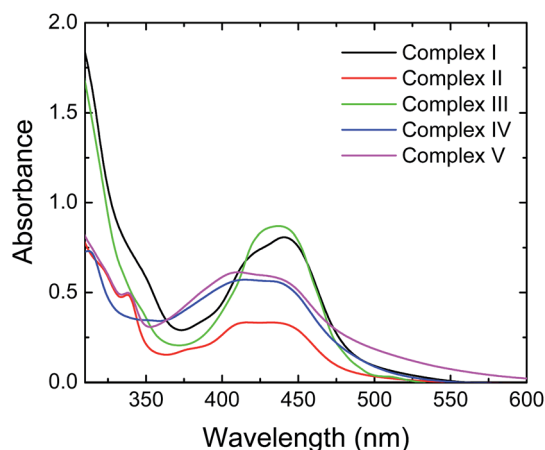
The electrochemical behaviors of the complexes in acetonitrile were investigated. The results are listed in Table 2. The cyclic voltammograms of the complexes contain one electron oxidation wave and one electron reduction wave. The oxidation potentials for all complexes range from 1.20 to 1.30 V due to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple, and the reduction potentials for all complexes range from –1.40 to –1.45 V, due to ligand reduction *versus* SCE (Table 2). The oxidation potentials of the complexes decrease in the order of coordinated ligands $\text{L}^2 > \text{L}^1 \approx \text{L}^3$, due to the presence of three conjugative electron-withdrawing nitrogen atoms (N–N–N) in L^2 . This observation characterizes the π^* acceptor properties of the three L ligands. The cyclic voltammogram of complex I is shown in Fig. 2.

Photophysical and photochemical properties

Photoluminescence. The complexes are all luminescent at room temperature. Luminescence spectra were obtained in acetonitrile solution and the absorption peak lies near 600 nm.

Table 1 Electronic,^a emission^a and electroluminescence spectral data of the complexes

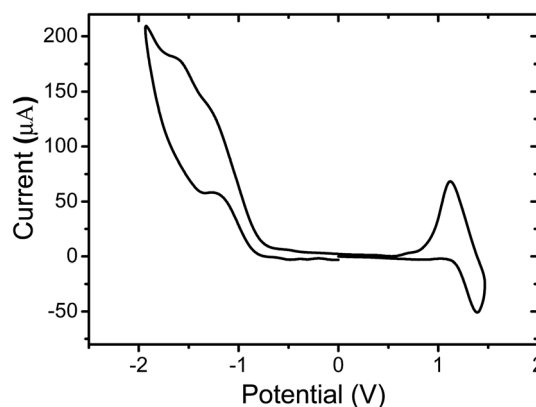
Compounds	Absorbance maximum, nm, (ϵ_{max} , 10^4) ($\text{M}^{-1} \text{cm}^{-1}$)	PL max. (nm) & quantum yield (life time, ns)		EL max. (nm)
[Ru(bpy) ₂ (L ¹)](PF ₆) ₂	444(1.29), 420(1.13)	603	0.0071 (129)	582
[Ru(bpy) ₂ (L ²)](PF ₆) ₂	447(0.95), 417(1.12)	598	0.0110 (142)	580
[Ru(bpy) ₂ (L ³)](PF ₆) ₂	445(1.11), 420(1.10)	602	0.0063 (115)	582
[Ru(phen) ₂ (L ¹)](PF ₆) ₂	441(1.10), 414(1.17)	585	0.0020 (17)	583
[Ru(phen) ₂ (L ²)](PF ₆) ₂	442(1.29), 414(1.17)	601	0.0001 (3)	575
[Ru(bpy) ₃](PF ₆) ₂ (ref. 28 and 46)	451(1.42), 345(0.650)	620	0.0420 (800)	609
[Ru(phen) ₃](PF ₆) ₂ (ref. 28 and 46)	447(2.30), 420(2.10)	589	0.0230	600

^a In acetonitrile at 298 K.**Fig. 1** Absorbance spectra of ruthenium complexes in acetonitrile solution.

Excitation spectral studies have demonstrated that the luminescence is associated with the above noted MLCT bands. The luminescence spectra are shown in Fig. 3. The [Ru(bpy)₂(L¹)]²⁺ and [Ru(bpy)₂(L³)]²⁺ complexes show very similar luminescence properties, which are weaker compared to their corresponding L² ligated analogues. The bipyridine co-ligated complexes are more luminescent than their phenanthroline co-ligated analogues. The maximum quantum yield is (*ca.* 0.011) in this family, slightly reduced compared to [Ru(bpy)₃]²⁺ (4d⁶) complex. This is opposite to the trend observed for Re(i) ligands, as [Re(L¹)(CO)₃Cl] has greater quantum yield compared to the [Re(bpy)(CO)₃Cl] (5d⁶).^{38,45} The photo-physical measurements

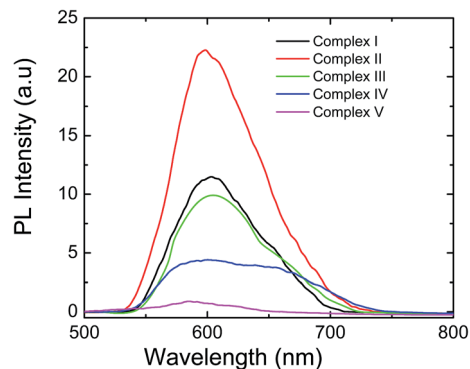
Table 2 Redox potentials of complexes in acetonitrile vs. SCE at 298 K

Compounds	Ru ^{II} /Ru ^{III} <i>E</i> (V), (ΔE_p , mV)	Ligand/ligand <i>E</i> (V), (ΔE_p , mV)
[Ru(bpy) ₂ (L ¹)](PF ₆) ₂	1.25 (70)	−1.41 (100)
[Ru(bpy) ₂ (L ²)](PF ₆) ₂	1.30 (80)	−1.40 (80)
[Ru(bpy) ₂ (L ³)](PF ₆) ₂	1.24 (80)	−1.43 (100)
[Ru(phen) ₂ (L ¹)](PF ₆) ₂	1.21 (90)	−1.42 (90)
[Ru(phen) ₂ (L ²)](PF ₆) ₂	1.31 (80)	−1.40 (70)
[Ru(bpy) ₃](PF ₆) ₂ (ref. 22, 47 and 48)	1.27(80)	−1.31 (70)
[Ru(phen) ₃](PF ₆) ₂ (ref. 28, 47 and 48)	1.19	−1.44

**Fig. 2** Cyclic voltammogram of [Ru(bpy)₂(L¹)](PF₆)₂ complex in acetonitrile solution at platinum working electrode (scan rate 100 mV s^{−1}).

are listed in Table 1. It is interesting to note that the pyridyl-triazine complex of ruthenium(II) with two bpy co-ligands is not photoluminescent, while the pyridyltriazine complex of ruthenium(I) with three carbonyls and a halide co-ligand is photoluminescent, despite the structural similarity of the triazine and triazolo rings.³⁸

Electroluminescence. To study the solid-state electroluminescence properties of the ruthenium complexes, we first measured the current–voltage and light–voltage characteristics of the thin film devices comprised only of the materials sandwiched between ITO and aluminum electrodes. Fig. 4 shows

**Fig. 3** Photoluminescence spectra of the complexes in acetonitrile solution.

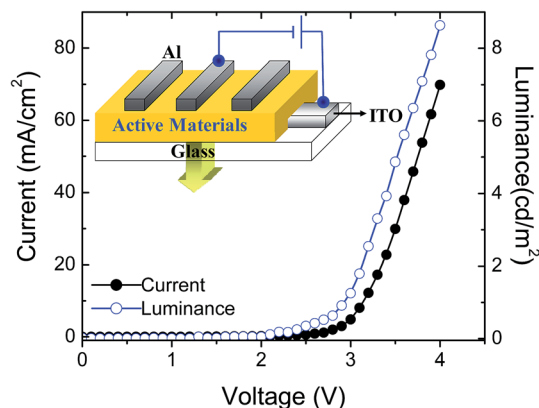


Fig. 4 Current–voltage (solid circle) and luminance–voltage (open circle) graphs of the ITO/ruthenium complex I/Al device. The schematic device structure is shown in the inset figure.

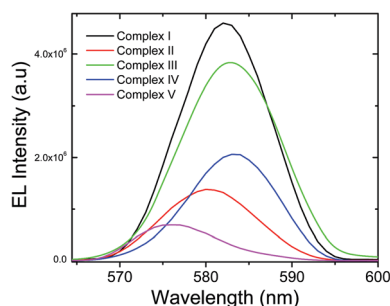


Fig. 5 Electroluminescence spectra of ITO/ruthenium complexes (I–V)/Al devices under 6.00 V bias.

light–voltage and current–voltage curves for a typical ITO/ruthenium complex I/Al device. In forward bias (ITO as the anode), devices turn on uniformly at relatively low voltages. The I – V characteristic of the devices shows asymmetric nature with high rectification ratio. The electroluminescence of the devices start at voltage 2.6 V and increases with the increase of the forward bias. It is also observed that the light emission in the reverse bias (ITO as cathode) is negligible in these devices. All the complexes are electroluminescent in nature. L^1 ligated complexes (I and IV) with bpy and phen coligands exhibit better electroluminescence properties compared to their L^2 ligated analogues (II and V). The complexes I and III show comparable electroluminescence and photoluminescence properties due to the similarity of L^1 and L^3 ligands with respect to the position of nitrogen in the heterocyclic rings. The L^1 and L^3 ligated complexes show weaker photoluminescence and stronger electroluminescence properties compared to their L^2 ligated analogue. Maximum brightness, about 8.6 cd m^{-2} at 4.00 V, was observed for complex I. Quantum efficiency of the devices is in the range of 0.02–0.04% photons/electron at 3.00 V, which is lower than the standard $\text{Ru}(\text{bpy})_3^{3+}$ complex at 3.00 V.²⁸

The electroluminescence spectra of the ruthenium complexes I–V are taken by applying 6.00 V forward bias, which are shown in the Fig. 5. Visible yellow light emission spectra were observed from these devices.

The response time of light-emitting electrochemical cells has always been a hindrance for their practical application. In general, the response time can be decreased by increasing the ionic conductivity of the ion-containing phase. This is especially effective in $[\text{Ru}(\text{bpy})_3]^{2+}$ type devices since the light emission and ion conduction occurs within the same phase. The ionic conductivity of $[\text{Ru}(\text{bpy})_3]^{2+}$ devices can be increased by changing the chemical structure of the $[\text{Ru}(\text{bpy})_3]^{2+}$ type complex or by decreasing the size of the mobile counter ions.²⁶

Conclusion

Here we report the spectroscopic, electrochemical, photo-physical and photochemical properties of a family of isoelectronic nitrogen rich cyclic aza-/azo-aromatic complexes of ruthenium. To the best of our knowledge, studies of electroluminescent devices incorporating this class of complexes have not been reported. While electroluminescent devices containing Ru(II) complexes of aryltetrazole ligands have been reported, the mode of binding of aryltetrazole ligands is different.

Although the highest photoluminescence efficiency of this family is slightly reduced compared to the parent $[\text{Ru}(\text{bpy})_3]^{2+}$ complex, the highest electroluminescence of this family is comparable to $[\text{Ru}(\text{bpy})_3]^{2+}$. The photoluminescence and electroluminescence properties of L^1 and L^3 ligated complexes are almost similar, whereas their L^2 ligated analogues exhibit different activities. So, the photo-physical and photo-chemical properties of this family depend mainly on nitrogen positions rather than the position of fused pyridine ring. From the present work, it is clear that in this particular family of ligands, increasing the number of nitrogen atoms in the heterocyclic ring reduces the photo-physical and photo-chemical efficiencies of the ruthenium complex based system significantly, unlike in the $[\text{Re}(L^1)(\text{CO})_3\text{Cl}]$ system, where increasing nitrogen atoms in the ligand framework results in greater quantum yield than the parent $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ (5d⁶). Also, transition metal complexes of iridium and platinum function efficiently as light-emitting self-assembled materials, despite containing a number of nitrogens in the heterocyclic ring. So the logical next step would be studying photo-redox properties of cyclometalated iridium and platinum metal complexes with a library of benzyl-triazolopyridine (isobars of pyridyltriazolopyridine) ligands, to explore the effects of different positions and numbers of nitrogen in the heterocyclic ring. That study is in progress.

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